

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C08F 2/06, 10/02	A1	(11) International Publication Number: WO 92/12182 (43) International Publication Date: 23 July 1992 (23.07.92)
(21) International Application Number: PCT/FI91/00406 (22) International Filing Date: 20 December 1991 (20.12.91) (30) Priority data: 906428 28 December 1990 (28.12.90) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, SF-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : AHVENAINEN, Antero [FI/FI]; Jousitie 2B A2, SF-06150 Porvoo (FI). SARANTILA, Kari [FI/FI]; Paimenpojantie 1, SF-06400 Porvoo (FI). ANDTSJÖ, Henrik [FI/FI]; Jousitie 29, SF-06150 Porvoo (FI). TAKAKARHU, Jouni [FI/FI]; Nummitie 20 C, SF-00760 Helsinki (FI). PALM-ROOS, Ari [FI/FI]; Haltiakuja 4 F 19, SF-04230 Kerava (FI).		(74) Agent: FORSSÉN & SALOMAA OY; Georgsgatan 30, SF-00100 Helsingfors (FI). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>

(54) Title: MULTI-STAGE PROCESS FOR PRODUCING POLYETHYLENE**(57) Abstract**

The invention concerns a multi-stage process for producing polyethylene having a bimodal and/or broad molecular weight distribution in the presence of an ethylene polymerizing catalyst system in a multistep reaction sequence, in which the first reaction step is a liquid phase polymerization step and the second reaction step is formed by one or more gas-phase polymerization steps. According to the process of the invention in the first reaction step ethylene is polymerized in a loop reactor (10) in an inert low-boiling hydrocarbon medium the residence time being at least 10 minutes, reaction mixture is discharged from the loop reactor (10) and at least a substantial part of the inert hydrocarbon mixture is separated and the polymere is transferred into one or more gas-phase reactors (30), where the polymerization is completed in the presence of ethylene and optionally hydrogen and a comonomer. As an inert hydrocarbon medium in the loop reactor (10) propane can be used and the polymerization can be carried out also so that the mixture of inert hydrocarbon, monomer, hydrogen and optional comonomer is under supercritical conditions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCI* on the front pages of pamphlets publishing international applications under the PCI.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TG	Togo
DK	Denmark			US	United States of America

Multi-stage process for producing polyethylene

5 The invention relates to a process for producing polyethylene having a bimodal and/or broad molecular weight distribution in a multi-stage process.

In certain applications, where films, bottles, cables and pipes are produced by extrusion or blow moulding, the polyethylenes having a narrow molecular weight
10 distribution are not satisfactory because of their low melt flow properties and poor processability. Therefore different approaches has been suggested for manufacturing polyethylenes having a broad molecular weight distribution.

One approach to widen the molecular weight distribution is to blend a low
15 molecular weight ethylene polymer with a high molecular weight ethylene polymer either mechanically or in solution. However according to this method it is very difficult to achieve sufficient homogeneity and/or expensive equipment is necessary for solution mixing, which makes these methods uneconomical and impractical.

20 Attempts have been made to broaden the molecular weight distribution by a proper selection of catalysts. However the degree of broadening the molecular weight by this way is rather small. Also the activity of the catalyst tends to decrease quickly and therefore it is necessary to remove the catalyst residuals by
25 washing.

There are also known various multi-stage processes for broadening the molecular weight distribution by carrying out the polymerization with using different hydrogen concentration in each stages. This can be achieved either by
30 polymerizing at a high hydrogen concentration at the first stage and at a low hydrogen concentration at the second phase, or vice versa. In the former case it is necessary to remove the unreacted gases and hydrogen after the first stage. In the latter case the conventional Ziegler-Natta catalysts tend to lose their activity

during the progress of polymerization already at the first stage. The rate of polymerization, which is initially high, decreases at the second stage reactor because of the lowered activity of catalyst and high hydrogen concentration. As a consequence the residence time in the second stage becomes much longer than in the first stage. This means larger size of reactor at the second stage and difficulties in the control of the whole process.

Different polymerization methods can be used in multistep processes. Known multistep processes are for example slurry-slurry processes, gas phase-gas-phase processes or slurry-gas phase processes. As examples of slurry-slurry processes can be mentioned US 3 592 880, EP 057 420, EP 237 294, GB 2 020 672, US 4 352 915 and EP 057 352. As examples of gas phase-gas phase processes GB 1 505 017, EP 040 992 and US 4 420 592 can be mentioned. As examples of slurry-gas phase processes GB 1 532 231, US 4 368 291, US 4 309 521, US 4 368 304 and EP 283 512 can be mentioned.

The present invention relates to a multi-stage process, in which slurry-gas phase process is used. Therefore the last mentioned group of patent publications is reviewed here with more detail to clarify the state of the art in this field.

GB 1 532 231 discloses a two-step liquid-gas phase process, where in the first stage an olefin is polymerized in liquid monomer. The liquid phase is partially separated from the polymer and the resulting concentrated mixture is transferred to the gas-phase reactor. Because in the slurry phase according to this publication the polymerization is carried out in liquid monomer, it is evident that this process cannot be used for ethylene polymerization. Another disadvantage in this process is the formation of solution of low molecular weight polymer in liquid monomer which causes problems related in product stream handling.

US 4 368 291 discloses a two-step liquid-gas phase process, in which an olefin is polymerized in liquid hydrocarbon medium in a stirred tank type reactor. After the first polymerization step the mixture containing polymer particles and liquid

hydrocarbon is as a whole transferred to the gas-phase reactor. One disadvantage of this process is that a great amount of hydrocarbon medium used in the first step is transferred to the gas-phase reactor disturbing polymerizing conditions there. The molecular weight control is also difficult in a conventional stirred tank
5 reactor. Separation of heavier diluent is also more difficult and uneconomical.

US 4 309 521 and US 4 368 291 concern special catalysts, which can be used in liquid-gas-phase processes. These publications do not afford any useful information about the processes as itself.

10

Lastly EP 283 512 concerns a multi-stage process using certain specified catalyst. According to this publication liquid propylene or other liquid olefin is first prepolymerized in a liquid-phase reactor, for example in a loop reactor, the residence time being from 10 seconds to 400 seconds, after which the
15 polymerization mixture as a whole is transferred to a gas-phase reactor, where polymerization is continued in gas phase. This process is thereby similar as GB 1 532 231 mentioned above and the process cannot be used in ethylene polymerization. The loop reactor step is merely a prepolymerization step. This patent publication is referred here only, because a loop reactor is mentioned in
20 connection with a gas-phase reactor.

This invention is based on a surprising discovery, that by using a loop reactor polymerization in inert low-boiling hydrocarbon (so-called light diluent process) together with gas-phase polymerization it is possible to achieve special advantages, which could not be possible by using conventional slurry-phase
25 polymerization together with gas-phase polymerization.

Accordingly it is an object of the invention to provide a process, which permits manufacturing polyethylene, which has bimodal and/or broad molecular weight
30 distribution and has therefore excellent melt characteristics and extrusion or mould properties. This is because the use of a loop reactor compared to conventional stirred reactors gives better heat transfer from the reaction mixture and

therefore more even temperature profile and a higher slurry density and therefore better mixing.

Further the use of loop reactor permits shorter residence times and as a consequence the catalyst has not time to inactivate considerably and the catalyst transferred to the gas-phase reactor is still very active. The use of a loop reactor also makes possible higher polymer melt flow index, because in a loop reactor higher hydrogen concentrations can be used and therefore it is possible to achieve more narrow molecular weight distribution in the product of slurry phase. A short residence time in combination with the flexibility of a gas phase reactor permits to manufacture a product with lower density and more easier quality changes. Further the use of a loop reactor in combination with one or more gas-phase reactors allows the use of various catalysts and thereby flexibility in selection of catalysts.

These objects are achieved in the multi-stage process according to the invention for producing polyethylene having a bimodal and/or broad molecular weight distribution in the presence of an ethylene polymerizing catalyst system in a multistep reaction sequence, in which the first reaction step is a liquid phase polymerization step and the subsequent reaction steps are one or more gas-phase polymerization steps. According to the invention in the first reaction step ethylene is polymerized in a loop reactor in an inert hydrocarbon medium with a residence time of at least more than 10 minutes, the reaction mixture is discharged from the loop reactor and at least a substantial part of the inert hydrocarbon medium is separated and the polymer is transferred into one or more gas-phase reactors, where the polymerization is completed in the presence of ethylene monomer and optionally hydrogen and/or comonomers.

Generally any polymerization catalyst suitable for production of ethylene polymers can be used in the process according to the invention. Such catalysts are for example Ziegler-catalysts, which contain a transition metal selected from groups IV, V or VI of the Periodic Table, used together with a cocatalyst, usually

an alkyl aluminium compound. Preferable transition metal is titanium and the catalysts may be unsupported or supported on an inorganic carrier such as silica, alumina or silica-alumina and the like.

- 5 Preferable catalysts are for example those disclosed in Finnish patent applications 905430, 902123, 901895, 900842, 906323, 905703, 895526, 894266, 893621, 892153 and 872459. However it is to be noted that the process according to the invention is not a catalyst specific process and therefore any catalyst giving appropriate activity and a controllable molecular weight can be used in the process according to the invention.

10 The first step in the process according to the invention is carried out in a loop reactor, into which inert hydrocarbon medium, ethylene, hydrogen, catalyst and optional comonomer are fed. The loop reactor can be of conventional design, which includes means for feeding various feed components to the reactor, means for circulating the polymer-hydrocarbon suspension through the reactor, heat transfer means for removing heat of polymerization and means for discharging polymer slurry from the reactor.

- 15 20 As a polymerization medium an inert low-boiling hydrocarbon can be used. Examples of the hydrocarbons are aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane and octane and alicyclic hydrocarbons such as cyclohexane and cycloheptane. It is also possible to use a mixture of any of the hydrocarbons mentioned above.

25 The catalyst, preferably as a hydrocarbon slurry and together with a cocatalyst, inert hydrocarbon medium, ethylene, hydrogen and optional comonomer are fed continuously to the loop reactor. The reaction mixture is continuously circulated through the reactor, whereby a slurry of particle form polyethylene and inert hydrocarbon is formed. The loop reactor conditions are selected so that at least 20%, but preferably 40-90% of the total production is polymerized in the loop reactor. The temperature is usually selected between 75-110 °C, preferably

between 85-100 °C. Higher temperatures can also be used provided that the temperature remains below the melting point of the polymer under the prevailing reactor conditions. The reactor pressure can be selected between 40-90 bar, preferably between 50-65 bar. The residence time should be at least 10 minutes, but preferably between 1-2 hours. The molar ratio of hydrogen to ethylene is selected depending among others on the melt index of the product desired, but in the manufacture of bimodal polyethylene it will be between 0-1.0.

Special advantages can be achieved if a hydrocarbon, preferably propane, under supercritical condition is used as inert hydrocarbon medium. This means that the reaction is carried out in such conditions, in which the temperature and the pressure are above the corresponding critical points of the reaction mixture formed by ethylene, propane, hydrogen and optional comonomer, but the temperature is lower than the melting point of the polymer formed. Thereby the temperature in the loop reactor will be between 85-110 °C and the pressure between 60-90 bar.

By using supercritical propane phase it is possible to use higher hydrogen concentrations as would be possible in subcritical conditions or by using isobutane or other hydrocarbons. The product has lower solubility and the separation of the hydrocarbon (propane) and hydrogen by flashing technique is more easy. In supercritical conditions there is in the reactor practically one single reaction fluid, where no separate liquid and gas phases can be detected, and this gives good heat transfer, free mixing of gas components in the fluid and a low viscosity of the reaction medium.

The reaction mixture is removed from the loop reactor either continuously or intermittently by conventional means. The inert hydrocarbon mixture as well as comonomer and hydrogen, if present, is removed from the polymer particles by conventional means, for example by flashing technique. The hydrocarbon medium, remaining monomers and hydrogen can be recycled back to the loop reactor.

The concentrated polymer mixture is then fed to a gas-phase reactor. This reactor can be a conventional fluidized-bed reactor, although other types of gas-phase reactors can also be used. In the fluid-bed reactor the bed comprises formed and growing polymer particles as well as catalyst components. The bed is kept in fluidized state by introducing gaseous components, such as ethylene monomer at a velocity enough to cause the particles act as a fluid. The fluidizing gas can include also inert carrier gases, such as nitrogen and also hydrogen, if desired as a modifying component.

10 The gas-phase reactor used in the second phase can be operated at a temperature range of 60-115 °C, preferably 70-110 °C. The pressure can be within the range of 10-25 bar the partial pressure of ethylene being 1-20 bar. The molar ratio of hydrogen to ethylene is preferentially lower than in the loop reactor. Thereby the hydrogen concentration in the gas-phase reactor can be between 0-15 10 mol-%.

It is also possible to feed various gaseous comonomers to the gas-phase reactor, if desired. These comonomers include for example propylene, 1-butene, pentene, 1-hexene, 1-octene or 4-methyl-1-pentene.

20

It is also preferable to use such gas-phase reactor, which is equipped with a mixer. It helps to keep the reactor surfaces clean and improves gas distribution into the reactor.

25 The invention is not limited to a two-stage process. Instead of one gas-phase reactor it is possible to use two or even three gas-phase reactors after the loop reactor.

30 The configuration of the process according to the invention is further illustrated by the Figure enclosed, in which a loop reactor is marked by reference number 10. The catalyst is fed from a catalyst reservoir 11 with the aid of a catalyst feeder 12 through the catalyst transfer line 13 to the loop reactor 10. Ethylene

from line 14, low-boiling hydrocarbon from line 15, hydrogen from line 16 and optional comonomer from line 17 are fed to the loop reactor 10 through line 18. In the loop reactor 10 the reaction mixture is circulated by proper circulation means (not disclosed) and at the same time polymerization heat is removed by
5 cooling the reactor or the reaction medium with a cooling system (not disclosed).

From the loop reactor 10 the polymer-hydrocarbon mixture is fed to a flash separator 20, through which one or more discharge valves 19 and a product discharge line 21. The hydrocarbon medium, remaining monomer and co-
10 monomer and hydrogen separated from the polymer particles are removed from the flash separator 20 through line 23 either to the diluent recovery system (not disclosed) through line 24 or recycled back to the loop reactor 10 through line 25. The polymer particles are removed from the flash separator through line 22 to the gas-phase reactor 30.

15 In the lower part of the gas-phase reactor 30 there is a bed of polymer particles, which is kept in fluidized state by blowing gaseous monomer, comonomer and hydrogen from line 32 to the bottom of the reactor 10 and through the gas distribution plate 31. Gaseous components are continuously removed from the
20 top of the reactor 30 and recycled through a cooling device 35, compressor 36 and line 37 and line 32 back to the bottom of the reactor 30. The reactor can be equipped with a mechanical stirrer 38 in order to keep the reactor surfaces clean. The product is removed intermittently or continuously from the gas-phase reactor 30 through line 39 to the product recovery system (not disclosed).

25 Although only one gas-phase reactor has been illustrated in the Figure, it is evident that it is possible to use two or even three gas-phase reactors in the process according to the invention as long as the first polymerization step is carried out in a loop reactor according to the claims.

30

The invention is further illustrated by the following examples.

Examples 1-8

In a two-phase polymerization of ethylene it was used a pilot-scale loop reactor having a capacity of about 50 kg/h and a gas-phase reactor having a capacity of about 75 kg/h including also the product coming from the loop reactor. In addition to ethylene it was used 1-butene as a comonomer in the loop reactor and 1-butene and 1-hexene in the gas-phase reactor. Hydrogen was used as a modifier. The catalyst added to the loop reactor was prepared according to example 1 in PCT-application FI90/00279. Propane and isobutane were used as a reaction medium in the loop reactor.

The gaseous components from the product coming from the loop reactor were removed into a flash tank, after which the product was transferred to the gas-phase reactor, where the polymerization was continued. Only loop reactor polymerization was studied in examples 2, 3, 7 and 8. The polymerization conditions and the product properties are disclosed in the following table.

With the process according to the invention it can be manufactured bimodal products having a controllable molecular weight distribution $D (M_w/M_n)$. In the examples 1, 4 and 6 the molecular weight distributions D of the products were 12, 9 and 23. According to the invention even more wide range can be achieved.

5 In normal unimodal products the corresponding D -values when Ziegler-type catalysts are used, are usually 3,5-6. In the process according to the invention the loop reactor produces products having a narrow molecular weight distribution. The D -values 3.5-4.0 measured in examples 2 and 4 are typical values.

10 From the products manufactured in examples 5 and 6 it was extruded pipes the processability being good. The pipes of example 6 were pressure tested by keeping the pipes in pressures of 5.3 and 4.3 MPa over 3200 hours (the tests still continuing), which shows good pipe strength. It is not possible to manufacture pipes having comparable properties from unimodal polyethylene.

15 The loop reactor process makes possible to use high hydrogen concentration, especially when supercritical propane is used as diluent. As observed when the examples 1, 5 and 6 were carried out, no formation of gas bubbles was detected. Melt flow index MFR_2 can be even as high as 260 without any problems

20 (Example 3).

With loop reactor it is possible to produce products having low density when supercritical propane is used as a diluent. The critical temperature of propane alone is about 92 °C and the critical pressure is about 45 bar (g). In the con-

25 ditions of Example 1 the critical temperature was about 85 °C and the critical pressure about 50 bar (g), which means supercritical conditions. When other hydrocarbons are used as reaction medium, the solubility prevents to achieve a density below about 945 kg/m³ (hexane diluent) or below about 935 kg/m³ (isobutane diluent). According to example 4 it is possible to achieve a density of

30 929 kg/m³ the melt flow being very high ($MFR_2 = 150$) without plugging of the reactor. When the example 7 was carried out it was observed that by using isobutane as diluent the reactor plugged the density being 936 kg/m³ and the

melt flow index MFR_2 being 1.7. When isobutane was used as the diluent, it was possible to achieve a density of 935 kg/m^3 melt flow index MFR_2 being lower (0.2), as example 8 shows.

Claims

1. Multi-stage process for producing polyethylene having a bimodal and/or broad molecular weight distribution in the presence of an ethylene polymerizing catalyst system in a multistep reaction sequence, in which the first reaction step is a liquid phase polymerization step and the second reaction step is formed by one or more gas-phase polymerization steps, characterized in that in the first reaction step ethylene is polymerized in a loop reactor (10) in an inert low-boiling hydrocarbon medium the residence time being at least 10 minutes, reaction mixture is discharged from the loop reactor (10) and at least a substantial part of the inert hydrocarbon mixture is separated and the polymer is transferred into one or more gas-phase reactors (30), where the polymerization is completed in the presence of ethylene and optionally hydrogen and a comonomer.
2. A process according to claim 1, characterized in that the polymerization in the first step is carried out for producing polymer having an increased melt index, and in the subsequent steps ethylene or ethylene and comonomers are polymerized for producing ethylene homopolymer or copolymer having a low melt flow index and low density.
3. A process according to claims 2, characterized in that the ratio of hydrogen to ethylene is within the range of 0-1 mol/mol, preferably within 0-0.5 mol/mol.
4. A process according to any of the preceding claims, characterized in that the inert hydrocarbon medium is selected from the group comprising propane, butane, pentane, hexane, heptane and octane.
5. A process according to claim 4, characterized in that the inert hydrocarbon medium is propane.
6. A process according to any of the preceding claims, characterized in that the

polymerization in the loop reactor (10) is carried out at a temperature of 75-110 °C and in the pressure of 60-90 bar.

5 7. A process according to any of the preceding claims, characterized in that the polymerization in the loop reactor (10) is carried out under supercritical conditions, whereby the polymerization temperature and pressure are above the corresponding critical points of the mixture formed by hydrocarbon medium, monomer, hydrogen and optional comonomer and the polymerization temperature is lower than the melting point of the polymer formed.

10

8. A process according to claim 7, characterized in that the polymerization in the loop reactor (10) is carried out in the temperature of 85-110 °C and in the pressure of 60-90 bar.

15

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 91/00406

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
IPC5: C 08 F 2/06; C 08 F 10/02

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷	
Classification System	Classification Symbols
IPC5	C 08 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in Fields Searched⁸

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A2, 0057420 (SUMITOMO CHEMICAL INDUSTRIES LTD) 11 August 1982, see page 14, line 22 - page 15, line 12; abstract; claims 1-2	1-8
A	US, A, 4368291 (FRESE ET AL) 11 January 1983, see column 1, line 67 - column 2, line 5; column 3, line 47 - line 53; column 3, line 61 - line 65	1-8
A	GB, A, 1532231 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 15 November 1978, see claim 1	1-8

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not
considered to be of particular relevance

"E" earlier document but published on or after the international
filing date

"L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or
other means

"P" document published prior to the international filing date but
later than the priority date claimed

"T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention

"X" document of particular relevance, the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step

"Y" document of particular relevance, the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

25th March 1992

Date of Mailing of this International Search Report

1992-04-01

International Searching Authority

SWEDISH PATENT OFFICE

Signature of Authorized Officer

Agneta Österman Wallin

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00406**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 28/02/92
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0057420	82-08-11	CA-A-	1162700	84-02-21
		GB-A-B-	2094810	82-09-22
		JP-A-	57126805	82-08-06
		JP-A-	57126808	82-08-06
US-A- 4368291	83-01-11	BE-A-	873692	79-07-24
		DE-A-C-	2803281	79-08-23
		FR-A-B-	2415642	79-08-24
		GB-A-B-	2016022	79-09-19
GB-A- 1532231	78-11-15	AU-B-	501040	79-06-07
		AU-D-	1282376	77-10-13
		BE-A-	840927	76-10-20
		DE-A-	2616699	76-10-28
		FR-A-B-	2322890	77-04-01
		JP-C-	1174960	83-10-28
		JP-A-	51135987	76-11-25
		JP-B-	56022443	81-05-25
		NL-A-	7603782	76-10-20
		US-A-	4187278	80-02-05
		US-A-	4291132	81-09-22